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# Fabrication of a polymer/mediator composite modified electrode and its application to electrochemical detection of iodate

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**Abstract**

A polymer/mediator composite modified glassy carbon electrode (GCE) is fabricated for electrochemical detection of iodate ($IO_3^-$). Flavin adenine dinucleotide (FAD) is chosen as mediator for sensing iodate, and 3,4 ethylenedioxythiophene (EDOT) is chosen for entrapping FAD and forming a conducting polymeric matrix, poly(3,4 ethylenedioxythiophene) (PEDOT). The PEDOT/FAD modification layer is electrodeposited on the GCE by cyclic voltammetric (CV) method. It is noted that FAD can enhance the electrodeposition of PEDOT, and possible reasons are proposed to explain this phenomenon. The optimal cycle number for preparing the modified electrode is determined to be 9. The relationship between the formal potential of FAD and the pH value is studied. Two slopes, 60.4 and 29.2 mV per pH unit, are recorded in the ranges of $1.5 \leqq pH \leqq 8.5$ and $8.5 \leqq pH \leqq 11.5$, respectively. Additionally, it is found that the oxidation current of iodate increases significantly with the decrease of pH value.


*Keywords*: Effect of pH value; Electrochemical detection; Flavin adenine dinucleotide; Iodate; Poly(3,4-ethylenedioxythiophene)

## 1. Introduction

Iodine is an essential component of thyroid hormones that play a vital role in the development of brain function and cell growth. Table salt is usually iodized with potassium iodate to prevent iodine deficiency disorders, such as mental retardation and endemic goiter. Nevertheless, excess intake of iodine can cause

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hyperthyroidism. Detecting iodate by electrochemical methods has several advantages, such as ease of operation, cost effective, and high sensitivity compared with traditional analytical methods. Fabrication of modified electrodes for detecting iodate has been endeavored for decades. Several materials have been utilized to enhance the sensitivity of the bare electrode, including metal oxides[1], polyoxometalates[2], and conducting polymers[3]. Recently, Marafon *et al.* have reported the binding of flavin adenine dinucleotide (FAD) onto $SiO_2/ZrO_2/C$ ceramic electrode to catalyze iodate reduction[4]. The sensitivity of their electrode, however, is comparatively low. In this research, we attempt to immobilize FAD by entrapping it into poly(3,4-ethylenedioxythiophene) (PEDOT) matrix, which also shows good catalytic ability toward iodate reduction[3]. Using a cyclic voltammetric (CV) method, we try to combine PEDOT with FAD as a composite material to modify the GCE.

## 2. Experimental

### *2.1. Chemicals and instrumentations*

3,4-ethlenedioxythiophene (EDOT, 97.0%), potassium chloride (KCl, ≧ 99.0%), flavin adenine dinucleotide disodium salt hydrate (FAD, ≧95.0%) are purchased from Sigma-Aldrich, Inc. (St. Louis, MO, USA). Polyethyleneglycol (PEG, 10000) is purchased from Alfa Aesar, Inc. (Boston, MA, USA). Potassium iodate ($KIO_3$, assay 100.2%) is obtained from J.T. Baker, Inc. (Phillipsburg, NJ, USA). Deionized water with a resistance ≧18.2 MΩ is produced by Purelab Maxima (ELGA, UK). All the chemicals are used as received. Electrochemical measurements are performed with a CHI440 electrochemical workstation (CH Instruments, USA) and the compatible software. A conventional three-electrode system is used. Glassy carbon electrode (GCE, diameter 3 mm) serves as a working electrode, platinum (Pt) wire as a counter electrode, and Ag/AgCl/sat'd KCl as a reference electrode.

### *2.2. Fabrication of the PEDOT/FAD modified GCE*

Before modification, the bare GCE is polished with alumina powder ($Al_2O_3$, 0.05 μm) and rinsed thoroughly with deionized water to obtain a mirror finish. The cleaned GCE is immersed in an aqueous solution containing 6.0 mM EDOT, 1.2 mM FAD, 25.0 mM KCl, and 0.2 mM PEG. The pH value of this solution is *ca.* 5.7. The electrodeposition of PEDOT/FAD modification layer is carried out by scanning between -0.5 and 1.1 V at 50 mV $s^{-1}$ for 9 cycles. After electrodeposition, the PEDOT/FAD modified GCE is placed in a buffer solution (which is purged with nitrogen for 15 min in advance) and scanned between 0.2 and -0.6 V at 100 mV $s^{-1}$ for 30 cycles in order to obtain a stable voltammogram.

## 3. Results and discussion

### *3.1. Fabrication of the PEDOT/FAD modified GCE and its electrocatalytic ability toward iodate*

It is our goal to combine PEDOT with FAD to modify the GCE. The initial cycle number chosen to prepare the modified electrode is 6. After electrodeposition, the modified electrode is scanned between 0.2 and -0.6 V in a buffer solution. Curve (e) in Fig. 1 shows a capacitance region and a pair of peaks, which belong to PEDOT and the redox reaction of FAD, respectively. This curve demonstrates the successful combination of PEDOT and FAD preliminarily. Comparing curve (e) with curve (c) in Fig. 1, a remarkable difference in the capacitance region is noticed. Possible reasons are proposed for explanation of this phenomenon. PEDOT bears positive charges during anodic electropolymerization and requires the doping of anions to achieve charge balance; FAD bears two negative charges in weak acidic

environment, and therefore has a strong tendency to dope into the PEDOT matrix. Curves (b) and (d) in Fig. 1 show that the bare GCE and the PEDOT modified GCE have only slight catalytic abilities toward iodate reduction, however, the PEDOT/FAD modified GCE shows an obvious change in the redox peaks of FAD after adding 4 mM iodate; the cathodic peak current density increment is *ca.* 8.41 μA $cm^{-2}$. These results indicate that PEDOT and FAD can be combined as a new composite material for sensing iodate.

Since we use CV method to fabricate the PEDOT/FAD modified electrode, the effect of cycle number on the sensitivity of the modified electrode is investigated. Fig. 2 exhibits the reduction current density of iodate on the PEDOT/FAD modified GCEs prepared by using different cycle numbers. At low cycle numbers, the amount of PEDOT/FAD deposited onto GCE is small, and therefore low sensitivities are obtained. At high cycle numbers, although much PEDOT/FAD is formed, FAD entrapped in PEDOT matrix can also become a barrier to electron transfer. The highest sensitivity of 2.37 μA $mM^{-1}$ $cm^{-2}$ is found at 9 cycles; this cycle number is used for preparing the modified GCE for further discussion.

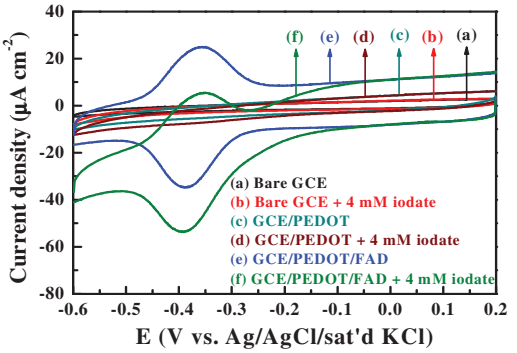


Fig. 1. Cyclic voltammograms of the PEDOT/FAD and PEDOT modified GCEs and the bare GCE with and without adding 4 mM iodate (background: pH 5.5 buffer solution; scan rate: 25 mV $s^{-1}$).

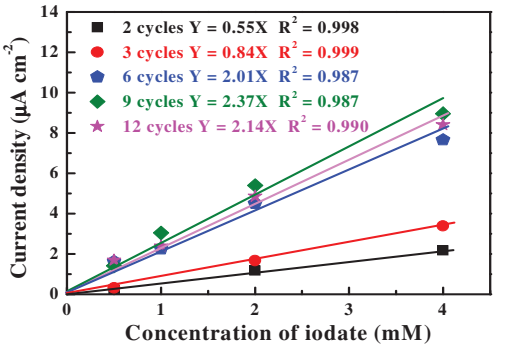


Fig. 2. Reduction current densities of iodate on the PEDOT/FAD modified GCEs prepared by different cycle numbers. This figure also lists the sensitivity of each modified electrode.

### *3.2. Effect of pH value on the performance of the PEDOT/FAD modified electrode*

In order to study the effect of pH value on the electrochemical performance of the PEDOT/FAD modified GCE, we perform CVs in buffer solutions with different pH values and select three of them for display. As shown in Fig. 3, the reduction peak current density of FAD decreases with the increase of the pH value, which can be explained as follows: the proton ($H^+$) is required in the reduction reaction of FAD. Increasing the pH value means decreasing the concentration of proton, and therefore the reduction peak current density of FAD decreases. Moreover, the capacitance region of PEDOT shown in curve (c) is smaller than those shown in curves (a) and (b); this implies that PEDOT is comparatively unstable in basic environments.

The dependency of the formal potential of FAD redox reaction on the pH value of buffer solution is studied. Two distinguished slopes can be observed in Fig. 4; one is 60.4 mV per pH unit, and the other is 29.2 mV per pH unit. By using the Nernst equation, it can be understood that FAD undergoes a two-electron- two-proton transfer process to become $FADH_2$ as the pH value ranges from 1.5 to 8.5, and a two-electron-one-proton transfer process to become $FADH^-$ as the pH value ranges from 8.5 to 11.5. The above results reveal that the redox behavior of FAD entrapped in the PEDOT film is similar to that of itself in aqueous solution[5], but is quite different from itself being covalently bonded on the electrode surface[4].

The effect of pH value on the reduction current of iodate on the PEDOT/FAD modified GCE is also investigated. The reduction current of iodate increases with the decreases of the pH value; the increment is even obvious as the pH value decreases from 3.5 to 1.5 (data not shown). Owing to the much higher reduction current at lower pH value, and the fact that the PEDOT/FAD modified GCE is more stable in acidic conditions, we choose pH 1.5 as the suitable condition for detecting iodate.

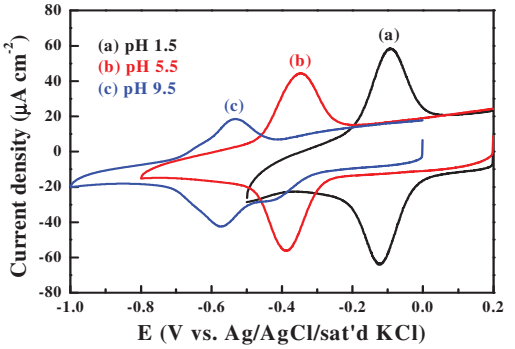


Fig. 3. Selected voltammograms of the PEDOT/FAD modified GCEs at different pH values (scan rate: 25 mV $s^{-1}$).

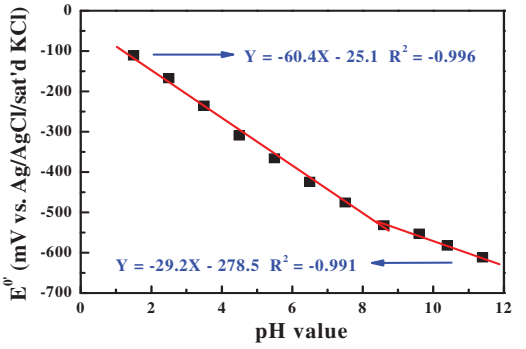


Fig. 4. The dependency of the formal potential of FAD redox reaction on the pH value.

## 4. Conclusions

The PEDOT/FAD modified GCE is successfully fabricated by using CV method. FAD is shown to enhance the electrodeposition of PEDOT because it bears two negative charges for doping. The relationship between the formal potential of redox reaction of FAD entrapped in PEDOT film and the pH value can be described by the Nernst equation. Since the reduction current of iodate increases significantly with the decrease of the pH value, we select pH 1.5 as the suitable condition for detecting iodate.

## Acknowledgements

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## References

[1] Kosminsky L, Bertotti M. Determination of iodate in salt samples with amperometric detection at a molybdenum oxide modified electrode. *Electroanalysis* 1999;**11**:623-6.

[2] Chen L, Tian X, Tian L, Liu L, Song W, Xu H. Electrochemical reduction and flow detection of iodate on $(Bu_4N)_2Mo_6O_{19}$ self-assembled monolayer. *Anal Bioanal Chem* 2005;**382**:1187-95.

[3] Balamurugan A, Chen SM. Flow injection analysis of iodate reduction on PEDOT modified electrode. *Electroanalysis* 2008;**20**:1873-7.

[4] Marafon E, Kubota LY, Gushikem Y. FAD-modified $SiO_2/ZrO_2/C$ ceramic electrode for electrocatalytic reduction of bromate and iodate. *J Solid State Electrochem* 2009;**13**:377-83.

[5] Verhagen MFJM, Hagen WR. Electron transfer mechanisms of flavine adenine dinucleotide at the glassy carbon electrode; a model study for protein electrochemistry. *J Electroanal Chem* 1992;**334**:339-50.